

Manifestation of the Jahn-Teller effect in elastic moduli of strontium fluorite crystals doped with chromium ions

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Abstract. Attenuation and phase velocity of ultrasound have been measured in strontium fluoride single crystal doped with chromium in the temperature range of 4 – 185 K at 56 -162 MHz. Anomalies have been found for all the normal modes corresponding to the non-vanishing elastic moduli of a cubic crystal. Interpretation of the observed anomalies has been done in the framework of relaxation in the system of Jahn-Teller (JT) complexes CrF_8 subject to full $T_{2g} \otimes (e_g + t_{2g})$ JT problem. Relaxation time has been calculated from the experimental data on ultrasonic attenuation and adiabatic and isothermal contributions of the impurity subsystem to the total elastic moduli have been obtained.

1. Introduction

Recent study of II-VI and III-V crystals doped with 3d metals with degenerate orbital states proved the efficiency of ultrasonic experiment for investigating properties of the Jahn-Teller (JT) centers [1] (see, e.g., [2-5] and references therein). It provides independent and sometime unique information about electronic structure, dynamics and local symmetry of point defects in addition to obtained by traditional methods such as electron spin resonance, pulse techniques using electron spin echo, electron spin envelope modulation spectroscopy [6-10], and other methods [11-14]. In contrast with



resonance methods, ultrasonic experiments deal with relaxation in the system of the JT impurities which occurs among equivalent JT distortions. The process of determination of relaxation contribution to total attenuation or elastic modulus should be done very accurately since theoretical description of JT effect (JTE) manifestation in an ultrasonic experiment relates only to the subsystem of the JT centers. However, the measured temperature dependence of attenuation $\alpha(T)$ is total attenuation which is represented as a sum of two components: the relaxation attenuation $\alpha_r(T)$ and the background one $\alpha_b(T)$. The last is assumed to be a smooth function (e.g., polynomial) in a wide temperature interval and coincides with $\alpha(T)$ at the ends of the interval. However, assumed form of $\alpha_b(T)$ is only approximation and nothing more which is desirable to be checked somehow.

One of the verification methods for the $\alpha_b(T)$ choice can be done with the help of the data on the temperature dependence of phase velocity v (or elastic modulus $c = \rho v^2$, where ρ is the density). It should be emphasized that the procedures of attenuation and phase velocity measurements are quite independent and are realized with different experimental methods. Moreover, the measurements of the phase velocity are almost independent of the bonding between the piezoelectric transducers and the studied specimen in contrast with the attenuation measurements and, therefore should be considered as more accurate ones. Thus, agreement of the results obtained with the help of these two independent techniques should serve as good confirmation of the $\alpha_b(T)$ choice.

The data on relaxation attenuation $\alpha_r(T) = \alpha(T) - \alpha_b(T)$ are used for determination of relaxation time τ . The dependence $\tau(T)$, in turn, provides information about the activation energy V_0 which is used for calculation the saddle points of the adiabatic potential energy surface (APES). Therefore, correctness of $\alpha_b(T)$ definition significantly influences on the final result.

At the same time, $\tau(T)$ obtained from data on attenuation can be used for calculation contribution of the impurity subsystem to the total dynamic elastic modulus c (dynamic means frequency dependent) and for construction the relaxed c^R and unrelaxed c^U versions of the modulus ($c^R = c_b + c_{JT}^T$ and $c^U = c_b + c_{JT}^S$, where c_b is the background modulus which represent the sum of all the subsystems except the JT one and assumed to be adiabatic modulus). Transformation from c^R to c^U takes place in the vicinity of the temperature T_1 which corresponds to the condition $\omega\tau(T_1) = 1$ (where ω is the cyclic frequency of the ultrasonic wave). So, the criteria of verification for the choice of $\alpha_b(T)$ and, consequently, criteria of correct $\tau(T)$ dependence should be: (i) shift of T_1 with frequency increase and (ii) asymptotic dependences of the dynamic moduli measured at difference frequencies at low temperature and high temperature (with respect to T_1) to c^R and c^U obtained at a certain frequency, since c^R and c^U are frequency independent versions of the modulus.

Temperature dependences of ultrasonic attenuation obtained for different normal modes in $\text{SrF}_2:\text{Cr}^{2+}$ were reported in [15]. The data on attenuation were used for calculation of relaxation time and evaluation of the extreme points of the APES for the full $T_{2g} \otimes (e_g + t_{2g})$ JT problem. Here we present new results on temperature dependences of the elastic moduli, prove the relaxation nature of the anomalies found at low temperatures and verify the choice of background attenuation using the method suggested above.

2. Experiment

2.1. Crystal properties

The single crystals of strontium difluoride were grown in Kazan E.K.Zavoisky Physical-Technical Institute of the RAS by Czochralski method in a helium atmosphere with addition of thermal decomposition products of Teflon. The chromium impurity was introduced into the melt as CrF_2 well-dried powder. A detailed study of the crystals [6] showed that the samples contain mostly centers of bivalent chromium.

Concentration of the impurities was determined in the Institute of Solid State Chemistry of the Ural Branch of the RAS by inductively coupled plasma mass spectrometer (ICP-MS) using quadrupole based instrument ELAN 9000 (Perkin-Elmer SCIEX) with standard operating and acquisition parameters. Chromium concentration proved to be $n_{\text{Cr}} = 1.6 \times 10^{19} \text{ cm}^{-3}$ and significantly exceeded concentration of all the other measured impurities (Fe, Cu, Ni, Y).

The Cr^{2+} dopants in cubic crystals with fluorite structure replace the Sr^{2+} ions in the lattice site of O_h symmetry and are surrounded by eight fluorine ions in the corners of the cube. The 5D term of a free Cr^{2+} ion is split by the cubic crystal field into the ground orbital triplet $^5T_{2g}$ and excited doublet 5E_g . Due to the JTE, the cubic coordination of the Cr^{2+} ion in the degenerate state $^5T_{2g}$ is unstable with respect to twofold e_g and threefold t_{2g} type displacements of the environment. In linear approximation of the vibronic coupling, the dominant interaction with one of these two types of displacements results in the tetragonal or trigonal minima of the APES. Account of the quadratic coupling terms leads to orthorhombic minima involving both trigonal and tetragonal local modes. Investigation of ultrasonic attenuation [15] proved that this case takes place in $\text{SrF}_2:\text{Cr}^{2+}$.

2.2. Ultrasonic experiment description

Ultrasonic experiments were carried out at Dresden High Magnetic Field Laboratory and at Ural Federal University with the help of setups operating as a frequency variable bridge. The ultrasonic waves propagating along the $[110]$ axis were generated and registered by LiNbO_3 piezoelectric transducers at the frequencies of 55-162 MHz. There are no degenerate normal modes propagating along this crystallographic direction and all the non-vanishing elastic moduli of a cubic crystal c_{11} , c_{12} and c_{44} can be measured. Attenuation and phase velocity of the modes were determined by corresponding elastic modulus, taken as a complex variable c_β : $\alpha_\beta = (1/2)(\omega/v_\beta) [\text{Im}(c_\beta)/\text{Re}(c_\beta)]$, $v_\beta = \text{Re} \sqrt{c_\beta/\rho}$, where index β denotes the type of the mode: one longitudinal $\beta = \ell$, and two shear waves: $\beta = T$ with polarization along $[111]$, $\beta = E$, $[1\bar{1}0]$. Accordingly, $c_\ell = (c_{11} + c_{12} + 2c_{44})$, $c_T = c_{44}$, $c_E = (c_{11} - c_{12})/2$. The $c_T = c_{44}$ modulus in the expression for c_β indicates that the wave produces trigonal distortions of the JT complex (i.e., distortions along the $\langle 111 \rangle$ type axis), whereas c_E indicates trigonal distortions (along $\langle 001 \rangle$). The expression for c_ℓ can be introduced in terms of symmetry moduli: $c_\ell = c_B + c_T + c_E/3$, where $c_B = (c_{11} + 2c_{12})/3$ is the bulk modulus describing the totally symmetric distortions. Thus, the local JTE e type mode manifests itself in attenuation and phase velocity of the shear wave polarized

along the $[1\bar{1}0]$ axis and in the longitudinal wave, whereas the local t_2 mode indicates the anomalies in longitudinal and shear wave polarized along the $[001]$.

2.3. Ultrasonic attenuation and evaluation of relaxation time

Figure 1 shows temperature dependences of ultrasonic attenuation for the mode related to the c_{44} modulus. Similar dependences but with smaller peaks were obtained for other normal modes.

To calculate the temperature dependence of relaxation time using the data on attenuation, one should subtract background attenuation from the measured one and derive the relaxation attenuation: $\alpha_r(T) = \alpha(T) - \alpha_b(T)$. For the data measured at 55 MHz we used $\alpha_b(T) = 1.73 \times 10^{-5} \times T^2 + 1.38 \times 10^{-8} \times T^4$. Relaxation time can be evaluated with the help of the following expression [2]:

$$\tau = \frac{1}{\omega} \left[\frac{\alpha_r(T_1) \cdot T_1}{\alpha_r(T) \cdot T} \pm \sqrt{\left(\frac{\alpha_r(T_1) \cdot T_1}{\alpha_r(T) \cdot T} \right)^2 - 1} \right]. \quad (1)$$

The signs before the square root should be chosen according to the statement that relaxation time is increased with temperature lowering. Relaxation time evaluated with the use of the data presented in figure 1 is given in figure 2.

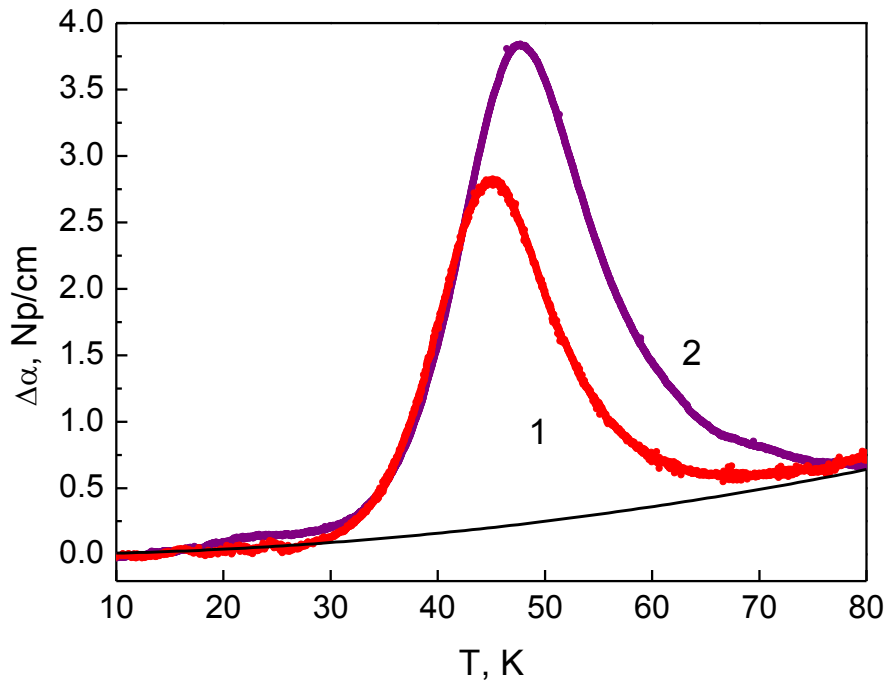


Figure 1. Temperature dependences of ultrasonic attenuation for normal mode related to the c_{44} modulus. Curve 1 was obtained at 56 MHz and curve 2 – at 105 MHz. $\Delta\alpha = \alpha(T) - \alpha(T_0)$, $T_0 = 4$ K is the reference temperature.

2.4. Dynamic, relaxed and unrelaxed moduli

Once we have relaxation time data, the relaxed and unrelaxed moduli can be evaluated [2]:

$$\frac{c^U - c_0}{c_0} = 2 \frac{\Delta\nu}{\nu_0} + 2 \frac{\alpha_r}{k_0} \frac{1}{\omega\tau}, \quad (2)$$

$$\frac{c^R - c_0}{c_0} = 2 \frac{\Delta\nu}{\nu_0} - 2 \frac{\alpha_r}{k_0} \omega\tau, \quad (3)$$

where $k_0 = \omega / \nu_0$ is the wave number, c_0 is dynamic modulus defined at $T_0 = 4 \text{ K}$, $\nu_0 = \nu(T_0)$, $\Delta\nu = \nu(T) - \nu(T_0)$.

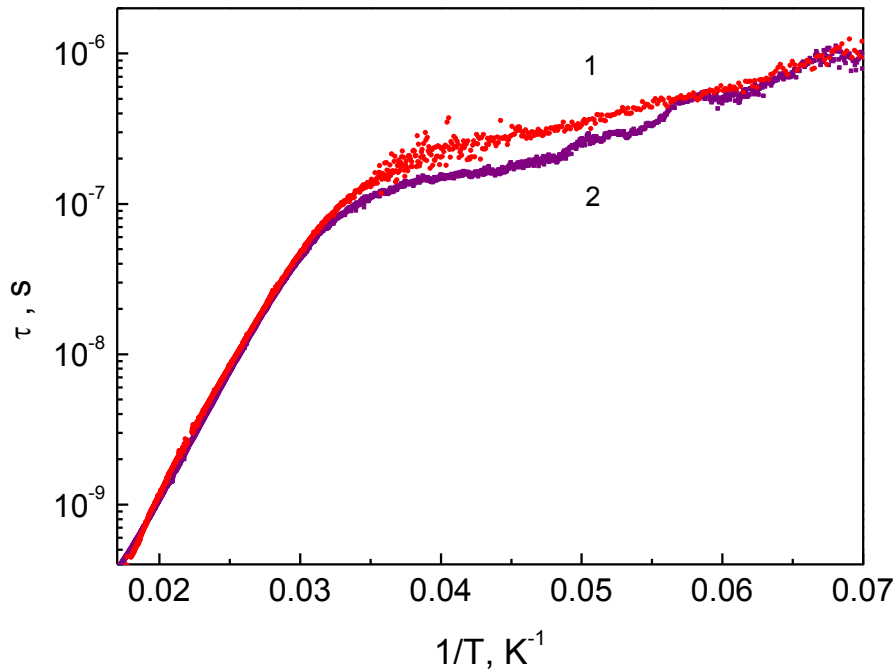


Figure 2. Temperature dependence of relaxation time obtained for normal mode related to the c_{44} modulus. Curve 1 was obtained at 56 MHz and curve 2 – at 105 MHz.

Figure 3 shows temperature dependences of the relaxed and unrelaxed c_{44} modulus obtained at 105 MHz. The data derived at 56 MHz for these versions of the modulus are the same within the accuracy of the measurements. Actually, it should be so, because c^R and c^U are frequency independent versions. In the contrast to them, dynamic modulus is frequency dependent and it manifests itself in transformation from one version to another at different temperatures for different frequencies of the wave.

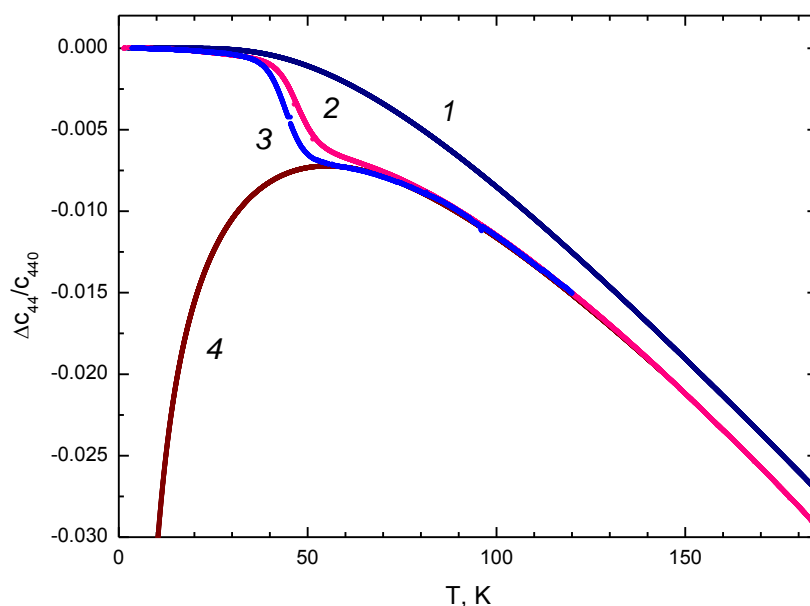


Figure 3. Temperature dependence of the dynamic modulus c_{44} (curve 2 – 105 MHz, 3 – 56 MHz), c_{44}^U (1 – 105 MHz), and c_{44}^R (4 – 105 MHz).

3. Conclusion

Attenuation and phase velocity in $\text{SrF}_2:\text{Cr}^{2+}$ were measured at 56 – 162 MHz in the temperature range of 4 – 185 K. Anomalies were found for the normal modes related to the elastic moduli $c_\ell = (c_{11} + c_{12} + 2c_{44})$, $c_T = c_{44}$, $c_E = (c_{11} - c_{12})/2$. The anomalies were interpreted as relaxation between equivalent JT distortions of the CrF_8 complexes. Relaxation attenuation was derived by subtracting the background attenuation (assumed as smooth function which has small variation at low temperatures) from the measured attenuation. Relaxation time was evaluated using the data on relaxation attenuation which in good agreement proved to be the same for different frequencies. This fact justifies the correct choice of the background attenuation. Using the data on phase velocity and relaxation time, the relaxed and unrelaxed versions of the moduli were evaluated. Obtained for different frequencies, they proved to be the same within the accuracy of the measurements. Transformation of the dynamic moduli from relaxed to unrelaxed versions measured at different frequencies occurred at different temperatures. This fact indicates good accuracy of $\alpha(T)$ and $v(T)$ measurements and proves the relaxation origin of the observe anomalies in temperature dependences of both attenuation and elastic moduli.

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References

- [1] Bersuker I B 2006 *The Jahn-Teller Effect* (Cambridge: Cambridge University Press)
- [2] Gudkov V V 2009 Ultrasonic Consequences of the Jahn-Teller Effect *The Jahn-Teller Effect* eds H Koppel, D R Yarkony, H Barentzen (Heidelberg: Springer) pp 746-766
- [3] Gudkov V V, Bersuker I B, Zhevstovskikh I B, Korostelin Yu V and Landman A I 2011 *J. Phys.: Condens. Matter* **23** 115401
- [4] Gudkov V V and Bersuker I B (2012) Experimental Evaluation of the Jahn-Teller Effect Parameters by Means of Ultrasonic Measurements. Application to Impurity Centers in Crystals *Vibronic Interaction and the Jahn-Teller Effect* eds M Atanasov, C Daul, P L Tregenna-Piggot (Heidelberg: Springer) pp 143-161
- [5] Averkiev N S, Bersuker I B, Gudkov V V, Baryshnikov K A, Zhevstovskikh I V, Mayakin V Yu, Monakhov A M, Sarychev M N, Sedov V E and Surikov V T (2014) *J. Appl. Phys.* **116** 103708
- [6] Zaripov M M, Tarasov V F, Ulanov V A, Shakurov G S and Popov M L 1995 *Fiz.Tverd. Tela* **37** 806
- [7] Oliete P B, Orera V M, and Alonso P J 1996 *Phys. Rev. B* **53** 3047
- [8] Oliete P B, Orera V M, and Alonso P J 1996 *Phys. Rev. B* **54** 12099
- [9] Hoffmann S K, Goslar J, and Lijewski S 2007 *J. Chem. Phys.* **127** 124705
- [10] Azamat D V, Dejneka A, Lancok J, Trepakov V A, Jastrabik L, and Badalyan A G 2012 *J. Appl. Phys.* **111** 104119
- [11] Oliveira G N P, Teixeira R, Mendonca T M, Silva M R, Correia J G, Lopes A M L and Araujo J P 2014 *J. Appl. Phys.* **116** 2239907
- [12] Yadav R, Nair H S, Kumar A, Adiga S, Bhat H L, Yusuf S M and Elizabeth S 2015 *J. Appl. Phys.* **117** 093903
- [13] Senanayake P S, Wells J-P R, Reid M F, Hughes-Currie R B, Berden G, Reeves R J and Meijerink A 2015 *J. Appl. Phys.* **117** 133109
- [14] Krivobok V S, Nikolaev S N, Bagaev V S, Pruchkina A A, Onishchenko E E, Kolosov S A, Klevkov Yu V and Skorikov M L 2016 *J. Appl. Phys.* **119** 055704
- [15] Zhevstovskikh I V, Bersuker I B, Gudkov V V, Averkiev N S, Sarychev M N, Zherlitsyn S, Yasin Sh, Shakurov G S, Ulanov V A and Surikov V T (2016) *J. Appl. Phys.* **119** 225108